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A REVIEW STUDY OF THE MICROSTRUCTURAL BEHAVIOR AND MECHANICAL PROPERTIES OF ZrB_2 ULTRA-HIGH TEMPERATURE CERAMIC

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ABSTRACT

Ultra high temperature ceramics are known for their good wear resistance, good oxidation resistance, high mechanical strength, extreme hardness, high thermal conductivity & good fracture toughness properties. These characteristics of ultra-high temperature ceramics made them ideal for high temperature applications. Therefore, ultra-high temperature ceramics are mostly used in aerospace application, thermal protection systems and for making sharp leading edges or nose tips in hypersonic re-entry vehicles. So, this paper reviews changes in microstructural behavior of ZrB_2& ZrB_2 based composites & their effects on mechanical strength, Flexural strength & oxidation resistance.

KEYWORDS: Zirconium Diboride (ZrB_2), Silicon Carbide (SiC), Polycarbosilane (PCS), EDM (Electron Discharge Machine) & Scanning Electron Microscopy (SEM)

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Original Article

1. INTRODUCTION

Ultra high temperature ceramics are the refractory ceramics which give excellent stable performance above 2000°C temperature. The ultra-high temperature ceramics are classified into diboride, carbide & nitride ceramics. Hafnium diboride (HfB2) & Zirconium diboride (ZrB_2) are the most widely used material in the thermal protection system and aerospace applications. Recent research has been carried out to modify & control micro structure of ultra-high temperature ceramics for producing highly pure metal which gives better performance under high temperature applications. There are certain limits for use of ZrB_2 as a single phase materials as it shows poor oxidation resistance, ablation resistance & poor damage tolerance in composites for high-temperature applications. To overcome this, addition of the SiC to ZrB_2 gives better results in a composites with improvement in oxidation resistance, ablation resistance & thermal shock resistance. The addition of SiC to ZrB_2 limits the grain growth because of which its mechanical strength, hardness, toughness as well as sintering of ZrB_2 improved. So in most of

the studies, with different percentage in volume SiC particles were added to ZrB_2. But later it was found that, the flexural strength of composites decreases as average size of SiC particles increases in the range of 1.2 to 3.1µmthe largest SiC grains acted as critical flows in microstructure which causing the failure of composites.

2. LITERATURE REVIEW

It was found from previous research that, compared to micron-sized SiC particles, nano-sized SiC particles with the ZrB_2 gives better mechanical results. When ZrB_2-SiC composites oxidised at 1473K with 30% weight of SiC, it exhibits the highest oxidation resistance. A fully dense composite structure can be obtained with the addition of oxide additives (i.e., addition of 1% volumeAl2O3+ 0.5% volume Y2O3 to ZrB_2based composites). Electro Discharge Machining (EDM) technique is useful for the manufacturing of the complex shape of ultra- high temperature ceramics. With the addition of PCS (Polycarbosilane) to ZrB_2 based composites its densification behavior remarkably improved.

In the previous literatures it was observed that, to improve oxidation resistance of ZrB_2, nano-sized SiC grains were used. The ZrB_2powder (~2.1 µm) &nano-ß SiC powder (~30nm) with 5, 10, 15, 20 vol % & ά-SiC powder(~6.4 µm) were ball milled together for 24 hours in ethanol under 200 RPM by using SiC milling media then the resulting slurry dried by using magnetic stirrer. The resulting mixtures hen proceed for hot pressing under a pressure of 30 MPa in a graphite dies at 2000°C in vacuum for 60 minutes then it cooled to 25°C & exposed in air at 1400°C for up-to 10 hours. The microstructures were analyzed by using SEM which are shown in below Figure 1(a), Figure 1(b), Figure1(c) &Figure1(d). The flexural strength was calculated by using four points flexural strength. [1,2].

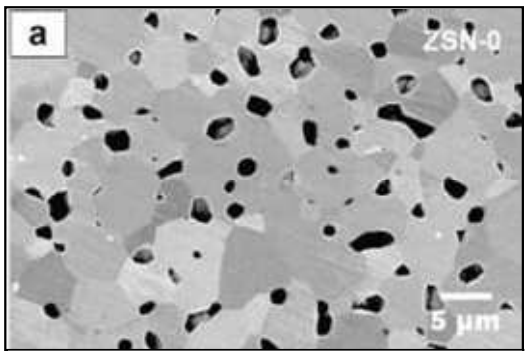

Figure 1(a): SEM Images of ZrB_2 with the Nano-Sized SiC Particles for ZSN-0

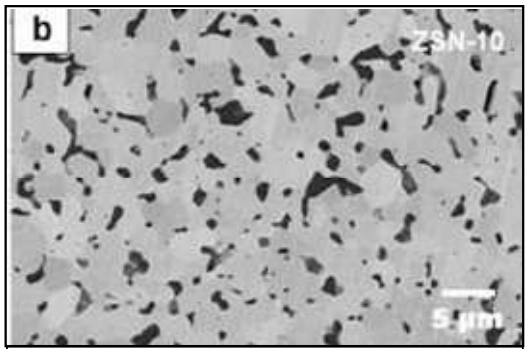

Figure 1(b): SEM Images of ZrB_2 with the Nano-Sized SiC Particles for ZSN-10

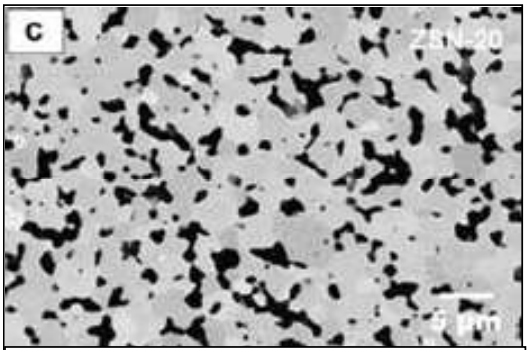

Figure 1(c): SEM Images of ZrB_2 with the Nano-Sized SiC Particles for ZSN-20

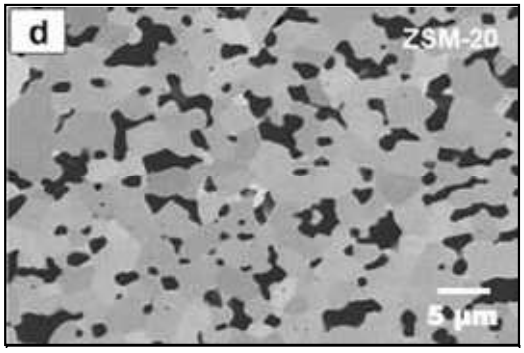

Figure 1(d): SEM Images of ZrB_2 with the Micron-Sized SiC Particles for ZSM-20

The obtained results for the grain size of the single-phase ZrB_2 & with the addition of 5 vol %nano-sized SiC to ZrB_2 were the same. So 5% volnano-sized SiC gave the grain size of 6.1µm were insufficient to hindering of the grain growth of the composites. With the addition of 10-20% vol of nano-sized SiC to ZrB_2 gave the average grain size of 4.2 to 4.5µm which is smaller than single phase ZrB_2. For reducing the grain size of ZrB_2 addition of 10-20% vol of nano-sized SiC is sufficient enough. Addition of micron size SiC to ZrB_2 gives the grain growth of size 5.4µm which is larger than nano-sized SiC particles.

When monolithic ZrB_2, with the addition of nano-sized SiC& addition of micron-sized SiC exposed to air at 1400°C for 10 hours results obtained listed in the table 1 below.

Table 1

Materials	4-Point Flexural Strength (MPa)	
	Pre-Exposed	Post-Exposed
ZSN-0	457 ± 58	141 ± 21
ZSN-5	549 ± 49	635 ± 15
ZSN-10	524 ± 63	610 ± 83
ZSN-15	714 ± 59	718 ± 82
ZSN-20	608 ± 93	700 ± 41
ZSM-20	531 ± 10	506 ± 19

It shows that monolithic ZrB_2 shows lower flexural strength before oxidation because of there is a porosity of 10%. The flexural strength of ZrB_2 with the addition of nano-sized ZrB_2 significantly improved. It is highest for 15% vol of nano-sized SiC particle that is up to 714 MPa. By comparing results obtained in 20% vol with nano-sized & micron-sized for exposed to air at 1400°C, nano-sized SiC particles show better results.

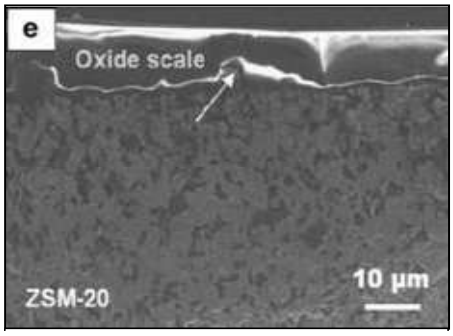

Figure 1(e): SEM Image of ZrB_2 with the Nano Sized SiC Particles after Oxidation Test for ZSN-20

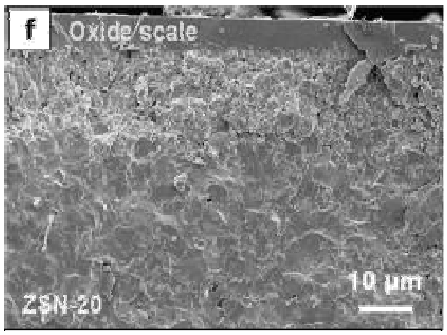

Figure 1(f): SEM Image of ZrB_2-with the Micron Sized SiC Particles after Oxidation Test for ZSM-20

When ZrB_2 with micron-sized SiC particles were oxidised it was observed with a thicker glassy layer as shown in Figure 1(e) between the oxide scale & bulk of ZrB_2 which causes a high level of defects because of which strength of ZrB_2 after oxidation decreased. When ZrB_2 with nano-sized SiC particles were oxidised it resulting in a thinner oxides scale as shown in Figure 1(f) because of which oxidation resistance of ZrB_2 increased.

The obtained results in this experiment are as follows.

- The addition of 5 % vol of nano-sized SiC to ZrB_2 is insufficient for hindering grain size of ZrB_2.
- The addition of 10-20 % vol of nano-sized SiC to ZrB_2 is sufficient for hindering grain size of ZrB_2& addition of micron sized SiC to ZrB_2 is also insufficient for hindering grain growth of ZrB_2.
- By comparing above three cases it is found that for hindering the grain growth of ZrB_2 based ceramics addition of nano-sized SiC particle is the more effective way.
- By comparing the strength for ZrB_2 with nano-sized SiC& for micron-sized SiC particles after oxidation exposure at 1400°C for 10 hours it is obtained that the strength for ZrB_2 with nano-sized SiC particles is higher as compare to micron-sized SiC particles There was a uniform distribution of nano-sized SiC particle within grains whereas in micron-sized SiC there were multiple grain pockets.
- Flexural strength of ZrB_2 with nano-sized SiC particles increases while flexural strength of micron size particles decreases. The presence of inter-granular & intra-granular nano-sized SiC particles improves oxidation resistance.

When ZrB_2oxidised above 1400° C, it formed volatile B2O3 which is porous in nature & offers poor oxidation resistance. It also formed a non-protective layer of ZrO2. To control this SiC is added with different percentage of vol to

ZrB_2 which forms borosilicate glass layer which is more viscous than B2O3& which offers better oxidation resistance. To study this behaviour experimentally Lihuna Zhang et al. used powder forms of ZrB_2 with 0%, 5%, 10%, 20%, 30% of vol of SiC& 1% wt of B 4C were taken as a raw material & mixed by ball mixing process then it was pressure-less sintered for 3 hours in air at 2523K in an Aratmosphere. The obtained specimens were polished with diamond abrasive up to 0.5mm finish & then inserted into an aluminium boat which will go into the higher temperature zone of a horizontal furnace where oxidation test carried out at 1273K& 1473K for 12 hours under an air atmosphere [4,7,11].

When ZrB_2-SiC composites oxidised at 1273K it forms a two oxide layer structure that is of a continuous glassy layer & of ZrO2 layer containing unoxidised SiC. With a 5% & 10%, wt of SiC contents a glassy layer formed composed of B2O3. With 20% & 30%, wt of SiC, borosilicate glass layer formed on the top of oxide layer which remarkably improve its oxidation resistance. SEM images after oxidation at 1273K are as shown in Figure 2(a) – Figure 2(e).

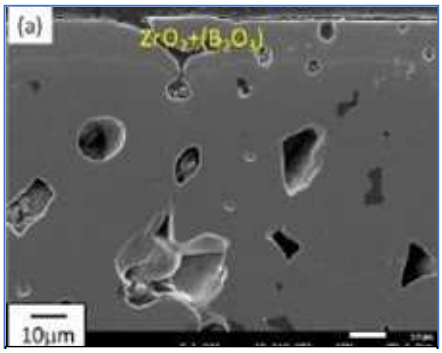

Figure 2(a): SEM Image of ZrB_2-SiC after Oxidation Test at 1273K in without SiC Addition

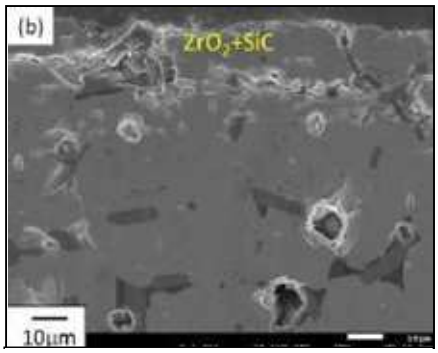

Figure 2(b): SEM Image of ZrB_2-SiC after Oxidation Test at 1273K in ZrB_2 with 5% SiC

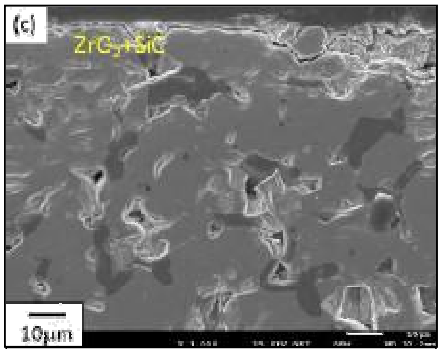

Figure 2(c): SEM Image of ZrB_2-SiC after Oxidation Test at 1273K in ZrB_2 with 10% SiC

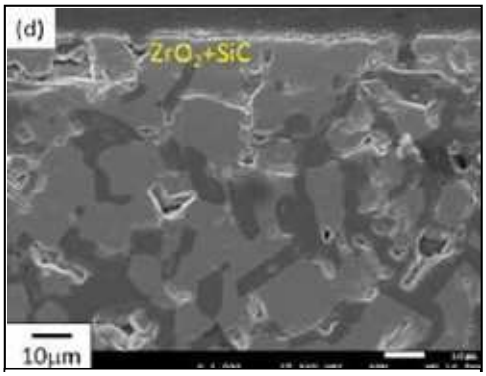

Figure 2(d): SEM Image of ZrB_2-SiC after Oxidation Test at 1273K in ZrB_2 with 20% SiC

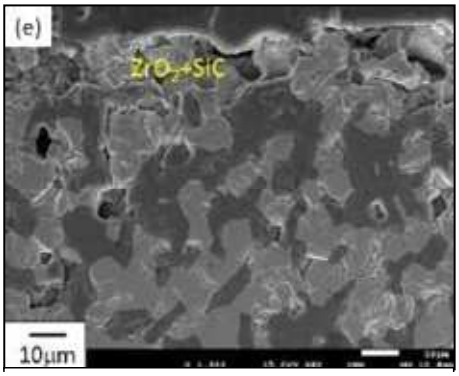

Figure 2(e): SEM Image of ZrB_2-SiC after Oxidation Test at 1273K in ZrB_2 with 30% SiC

When ZrB_2-SiC composites oxidised at 1473K, it forms a oxide layer which is consisting of ZrO2& SiO2 with unreacted SiC. With 10% weight SiC, a continuous borosilicate glass layer formed which help to improve oxidation resistance. SEM images after oxidation at 1473K are as shown in below from Figure 2(f) - Figure 2(i).

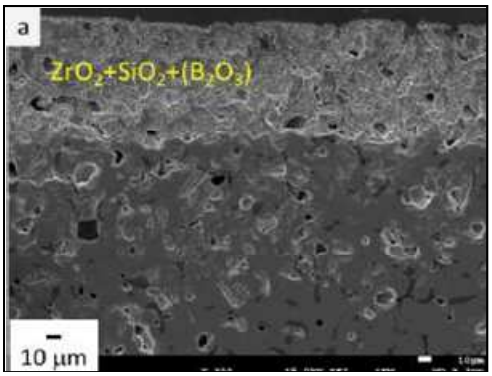

Figure 2(f): SEM Images of ZrB_2-SiC after Oxidation Test at 1473K in ZrB_2 with 5% SiC

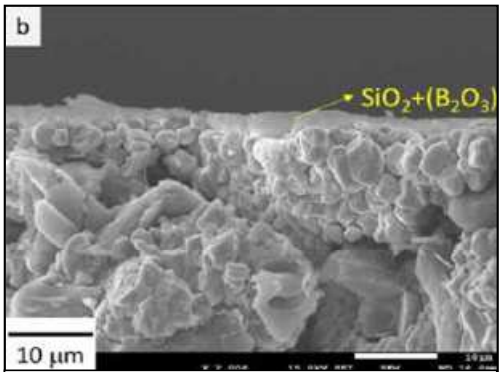

Figure 2(g): SEM Images of ZrB_2-SiC after Oxidation Test at 1473K in ZrB_2 with 10% SiC

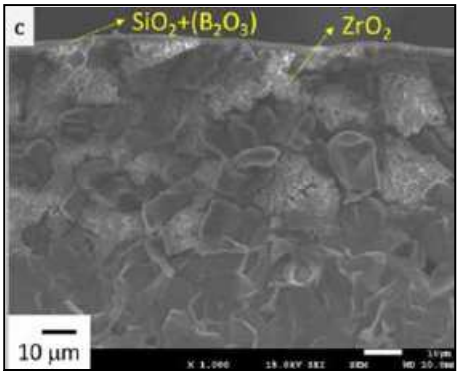

Figure 2(h): SEM Images of ZrB_2-SiC after Oxidation Test at 1473K in ZrB_2 with 20% SiC

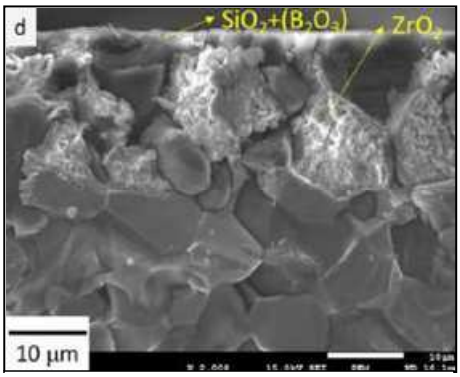

Figure 2(i): SEM Images of ZrB_2-SiC after Oxidation Test at 1473K in ZrB_2 with 30%SiC

With increasing % of SiC thickness of the oxide layer decreases in both the cases as shown in Figure 2(j) & Figure 2(k).

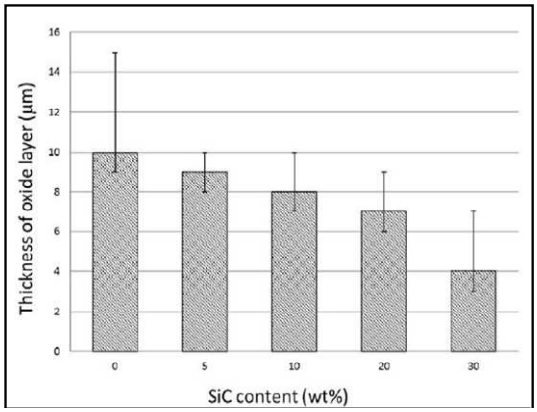

Figure 2(j):Thickness of Oxide Layer of ZrB_2-SiC after Exposure to Air for 12 h at 1273 K

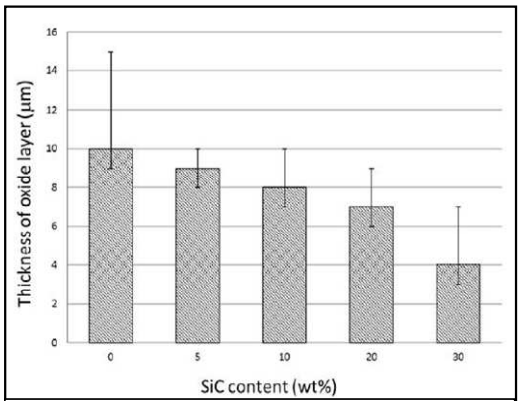

Figure 2(k): Thickness of Oxide Layer of ZrB_2-SiC after Exposure to Air for 12 Hours at 1473K

Another way to improve the properties of ZrB_2 is the addition of additives. Monteverde et al. Used monolithic ZrB_2 powder & ZrB_2 20% vol SiC composites for these experiments. Here ZrB_2 powder was hot pressed directly under the pressure of 30MPa at 1900°C for 30 minutes in BN-lined graphite dies containing a vacuum. In the mixture of ZrB_2-SiC, 5% vol Si3N4& oxides(1% vol Al2O3+0.5% vol Y2O3) were added as a sintering aid, then all mixtures were mixed together in ethanol for 20 hours by using silicon nitride balls and then dried in a rotary evaporator which containing continuous steam of Nitrogen. The obtained powder subjected to pressure less sintering and then hot pressed. Microstructure changes were analysed by using SEM shown in figure 3(a), figure 3(b), figure 3(c), & figure 3(d).[3,5].

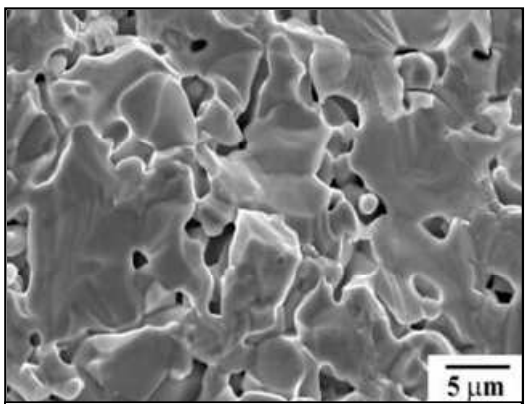

Figure 3(a): SEM Image of Additive Free ZrB_2

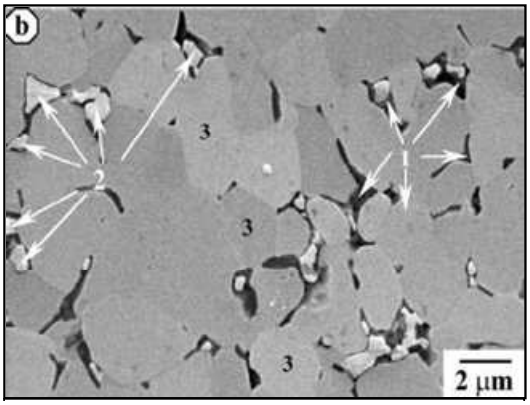

Figure 3(b): SEM Image from Fracture Polished Surface

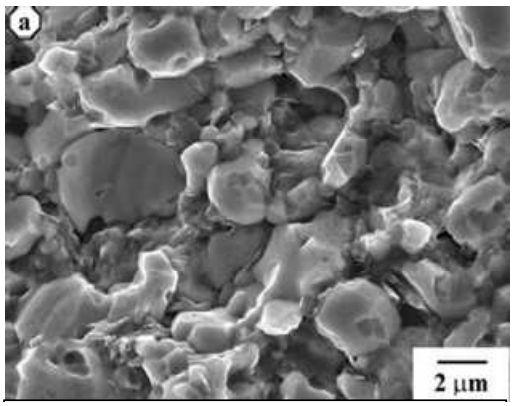

Figure 3(c): SEM Image of Material ZrB_2– SiC+ 5% Vol of Si_3N_4

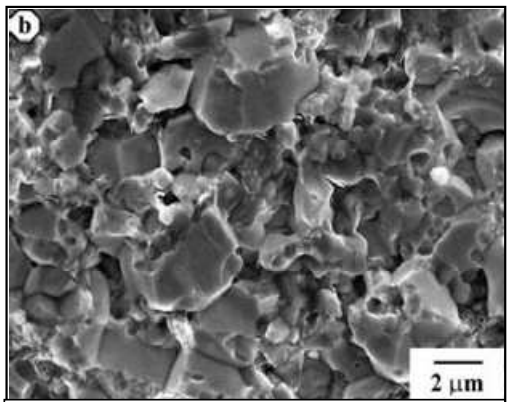

Figure 3(d): SEM Image of Material ZrB_2-SiC, 5% Vol Si3N4 + 1% Vol Al2O3+0.5% vol Y2O3

The microstructure of monolithic ZrB_2 obtained homogeneous in nature which is fully dense. It consisting of fine regular ZrB_2 grains with various grain boundary phases as shown in Figure 3(a). The addition of 5% volume of silicon nitride improves the sintering behavior of ZrB_2. A fully dense composites can be obtained at lower hot pressing temperature by addition of oxides to the mixture. Compared to monolithic ZrB_2, the addition of sintering aid improves the strength & sintering ability of composites.

In Figure 3(b), the darker regions (marked as 1) consist primarily of low density secondary phases, whilst the brighter ones (marked as 2) ZrO2. Areas associated to changing grey contrast correspond to ZrB_2 grains (marked as 3).

The obtained results in this experiment are as follows:

- The microstructure of monolithic ZrB_2 obtained homogeneous in nature with hardness value of 600 MPa& toughness value of 400 MPa at 25°C & 1000°C respectively.
- Addition of 20% vol of SiC to ZrB_2 forms a strong composites with hardness value of 710 MPa& toughness value of 630 MPa at 25°C & 1000°C respectively. So the composites become harder by 9% & tougher by 21%.
- By addition of oxides to ZrB_2 fully dense composites can be obtained at lower hot pressing temperature.

Another way to study the microstructure of ultra-high-temperature ceramics is by using polycarbosilane as a precursor. Raw materials were used in these experiments were ZrB_2 (97% purity) with 0%, 5%, 16% vol of SiC. ZrB_2 added into gasoline containing dissolved PCS. The mixtures were mixed together by ball milling for 24 hours. Pyrolysed mixture then hot pressed for 60 minutes at 2073k under a pressure of 20 MPa. The hardness & toughness were measured by using indentation after polishing the surface. Microstructure were analysed using SEM are shown in figure 4(a), figure 4(b), figure 4(c) & figure 4(d) [8,10].

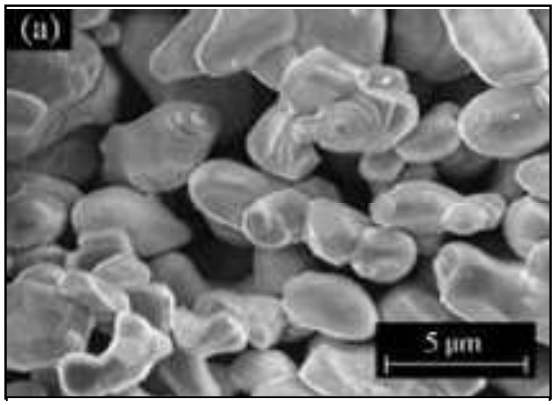

Figure 4(a): SEM Image of Powder of ZrB_2

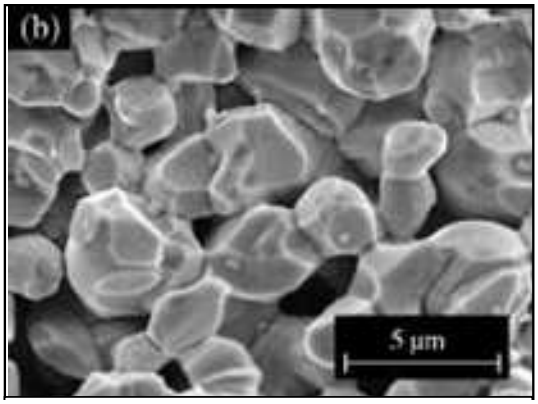

Figure 4(b): SEM Image of Sample S-0

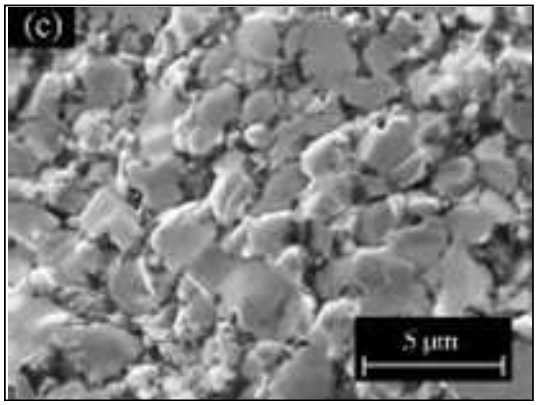

Figure 4(c): SEM Image of Sample S-5

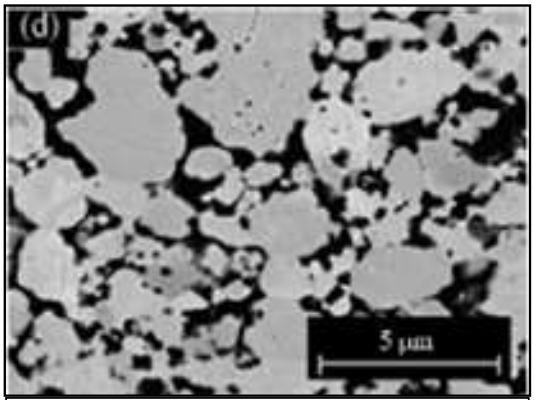

Figure 4(d): SEM Image of Sample S-16

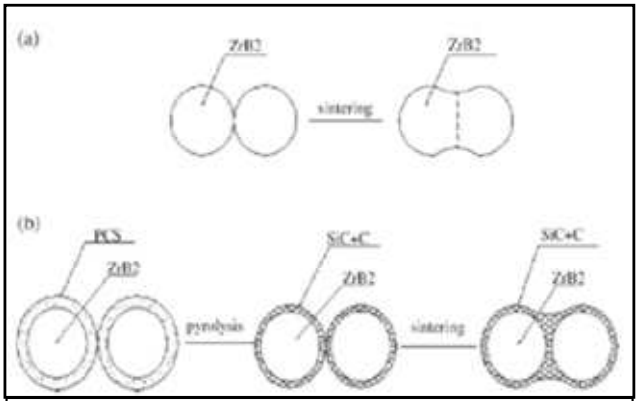

Figure 4(e): Microstructure Development for (a) Pure ZrB_2 Sample S-0 and (b) Samples with PCS

Pyrolysed PCS was amorphous in nature below 1073K & with increment in temperature above 1273K it get converted to ß-SiC& amorphous C. Schematic development is shown in figure 4(e). The SiC& C derived from PCS were homogeneously distributed in the ZrB_2 composites.

The obtained results in this experiment are as follows.

- Sample with 0% vol of SiC shows a relative density of 78% which found porous in nature with. ZrB_2 grains bonded together to form a network structure.
- Sample with 5% vol of SiC shows a relative density of 90% & Sample with 16% vol of SiC found fully dense.

Ultra-high temperature ceramics are mainly used to manufacture a sharp shape hot structure. To produce the machining ultra- high-temperature ceramics sintered pieces into more complex components EDM technique is an effective tool. Hot structure components can be prepared by using powder-mixture of ZrB_2 with 15% vol of SiC mixtures mixed in a non-aqueous medium using SiC milling balls. Dried in a rotary evaporator under a continuous stream of inert gas then hot pressed in an induction heated graphite dies at about 20°C/minutes of heating rate. From this mixture prototype of 10×12 cm is prepared (as shown in Figure 5(a)) which is subjected to EDM [6, 9].

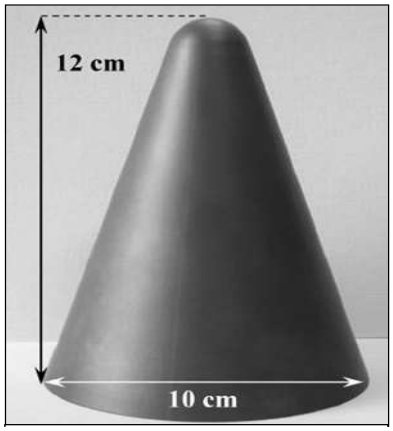

Figure 5(a): Ceramic Prototype Shape through the EDM Technique

EDM introduced the formation of a thin layer like Cu & Zn. During EDM microcracks are generated (as shown in figure 5(b) & figure5 (c)) on the surface due to electrical discharge action which decreases the flexural strength by 26.4%. EDM technique is basically design to form a thermal structure.

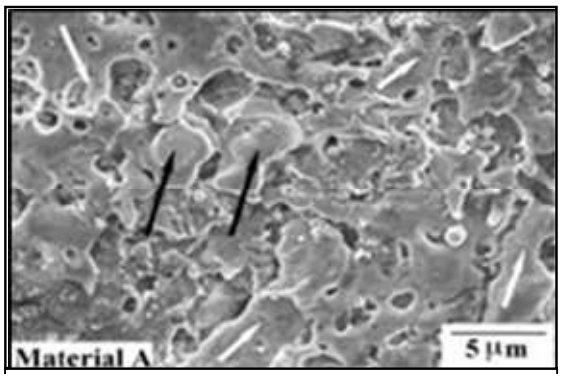

Figure 5(b): Electron Discharge Machined Surface of Material A

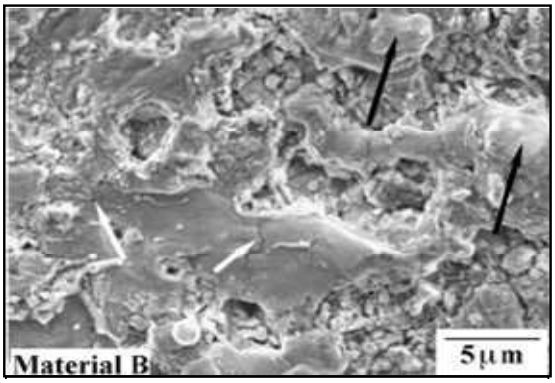

Figure 5(c): Electron Discharge Machined Surface of Material B

3. CONCLUSIONS

After studying changes in microstructural behavior of ZrB_2, the concluding remarks are as follows:

- After exposed in air at 1400°C for 10 hours, the strength of ZrB_2 with nano-sized SiC particles increased because of uniform distribution of nano-sized SiC particles in grain boundaries. The flexural strength of ZrB_2-based composites with nano-sized SiC particles increased compared to micron-sized SiC particles.
- Compared to oxidation at 1273K & 1473K, when ZrB_2-SiC composites oxidised at 1473K with 30% weight SiC exhibits the highest oxidation resistance. With the increasing % SiC in both the cases the thickness of the oxide layer decreases.
- Addition of oxide additives to ZrB_2-based composites gives composites which is fully dense at the lower hot pressing temperature(1760°C)
- The EDM technique can be used to produce a more complex shape of ultra-high temperature ceramics.
- With the addition of PCS densification property of ZrB_2-based composites improved. Before the addition of PCS relative density of the sample was 78% which converted to 100% after the addition of PCS under the same condition.

REFERENCES

1. *Shu-Qi Guo, Jenn M.Y., Hidehiko T., Yutaka K., (2008), 'Effect of thermal exposure on strength of ZrB_2-based composites with nano-sized SiC particles', Composites Science & Technology, 68, 3033-3040.*
2. *Shu-Qi Guo,(2009),'Densification of ZrB_2-based composites & their mechanical & physical properties: A review', Journal of the European ceramics Society,29,995-1011.*
3. *Tian, J. L., Zhang, H. Y., Wang, G. G., Wang, X. Z., Sun, R., Jin, L., & Han, J. C. (2015). Influence of film thickness and annealing temperature on the structural and optical properties of ZnO thin films on Si (1 0 0) substrates grown by atomic layer deposition. Superlattices and Microstructures, 83, 719-729.*
4. *Guo-J. Z.,(2009),'Ultra high temperature ceramics based on ZrB_2 & HfB2 systems: Powder sysnthesis, densification & mechanical properties', Journal of Physics: Conference series 176.*
5. *Trederic M., Raffale S., (2007),'Stability of ultra-high temperature ZrB_2-SiC ceramics under simulated atmospheric re-entry condition', Journal of the European Ceramics Society,27, 4797-4805.*
6. *Thomas H.S., Jochen M.,(2010),'Material property requirements for analysis & design of Ultra high temperature ceramics components in hypersonic applications', Journal of the European ceramics Society,30,2239-2251.*
7. *Bedjargi, P. R. C., & Kulkarni, R. SDS-Page Analysis and electron microscopy of corpuscles of stannius secretion in the freshwater fish, notopterus notopterus.*
8. *Sufang T., Jingyi D., Shijun W., Yang K.E.,(2007),'Ablation behaviour of Ultra high temperature ceramic composites', Material Science & Engineering A, 465,1-7.*
9. *Xiang Y., Wang S., Zhang B.F., Chen Z.H,(2013),'ZrB_2/SiC as a protective coating for C/SiC composites: Effect of high temperature oxidation on mechanical properties & ablation properties', Composites Part B, 45, 1391-1395.*

10. *Xion J. Z., Guo-J. Z., Yao G.L., (2006). 'Hot pressed ZrB_2-SiC-C ultra-high temperature ceramics with polycarbosilane. Materials letters', 61(2007), 960-963*

11. *El-Fadaly, E., Mostafa, M. R., Saraya, M., Nassar, F., & El-Sokkary, T. (2014). Eco-Friendly cement from ceramic waste geopolymarization. International Journal of Research in Applied, 2.*

12. *Monteverde, F.,Bellosi A., Lungi S.,(2007). 'Processing & properties of ultra-high temperature ceramics for space applications', Material Science & Engineering A, 415-421.*

13. *Sylvia M., Matt G., John L., (2018). Recent developments in ultra-high temperature ceramics at NASA Ames. NASA Ames Research centre, CA 94035.*

14. *Zhang, Lihua, Kurakawa, Kazuya,(2016).'Effect of SiC addition behaviour of ZrB_2 at 1273K & 1473K',Oxidation of metals,85(3-4), pp.311-320.*